A flexible supramolecular porous host with a crowned chair octameric water cluster and highly selective adsorption properties

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Table S1 Selected Bond Distances [Å] and Angles [deg] for **1**

Fe1-C5	1.945(7)	Fe1-C1	1.921(9)
Fe1-C6	1.938(7)	Fe1-C2	1.955(7)
Fe1-C3	1.943(7)	Fe1-C4	1.937(8)
C2-Fe1-C5	178.8(3)	C2-Fe1-C6	89.5(3)
C3-Fe1-C4	88.0(3)	C3-Fe1-C5	91.3(3)
C3-Fe1-C6	179.1(3)	C4-Fe1-C5	87.5(3)
C4-Fe1-C6	91.3(3)	C5-Fe1-C6	89.3(3)
C1-Fe1-C2	87.9(3)	C1-Fe1-C3	91.2(3)
C1-Fe1-C4	179.3(3)	C1-Fe1-C5	92.3(3)
C1-Fe1-C6	89.4(3)	C2-Fe1-C3	89.9(3)
C2-Fe1-C4	92.3(3)	Fe1-C1-N1	179.3(7)
Fe1-C2-N2	179.8(8)	Fe1-C3-N3	179.8(8)
Fe1-C4-N4	178.4(6)	Fe1-C5-N5	178.6(7)
Fe1-C6-N6	179.0(5)		

Table S2 Geometrical Parameters (Å,°) of Hydrogen Bonds for the Water Octamer[a]

O1W···O5W#1	2.692(8)	O1W--H2W···O5W	167.00
O2W···O6W#2	2.737(8)	O2W--H4W···O6W	172.00
O4W···O1W#3	2.750(8)	O4W--H7W···O1W	174.00
O4W···O3W#3	2.750(9)	O4W--H8W···O3W	174.00
O5W···O8W	2.738(8)	O5W--H10W···O8W	180.00
O6W···O4W	2.732(9)	O6W--H12W···O4W	179.00
O8W···O7W#4	2.750(8)	O8W--H15W···O7W	160.00
O8W···O2W#4	2.713(9)	O8W--H16W···O2W	158.00

[a] Symmetry: (#1) x, 1 + y, z; (#2) x, -1 + y, z; (#3) -1 + x, y, z; (#4) 1 + x, y, z.

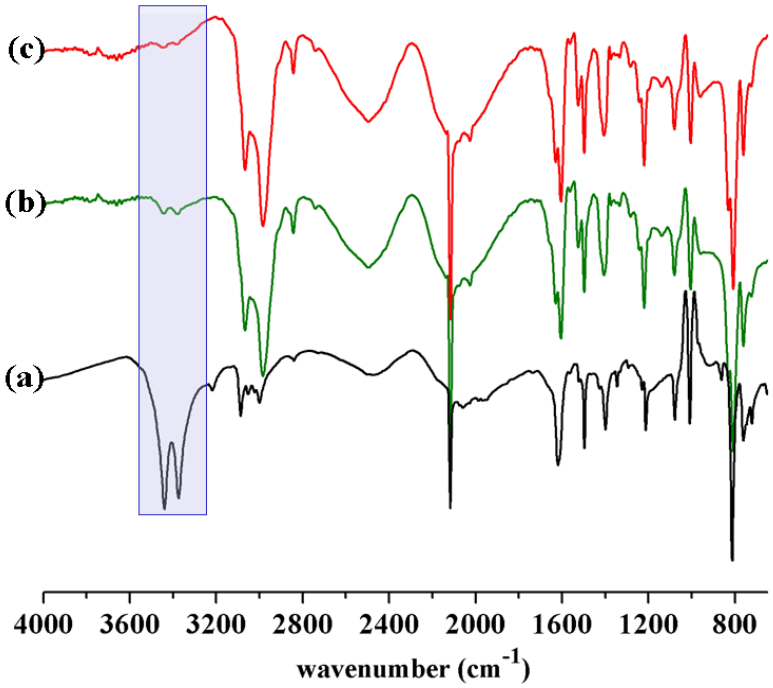

Fig. S1 IR spectra of compounds **1**(a), **1a** (c) and **1b** (b).

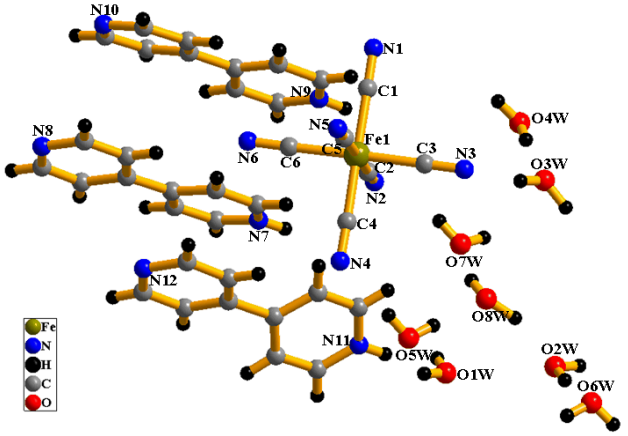

Fig. S2 View of the asymmetric unit of supramolecular host **1** shows one molecule of $[Fe(CN)_6]^{3-}$, three protonated bipy molecule and eight lattice water molecules.

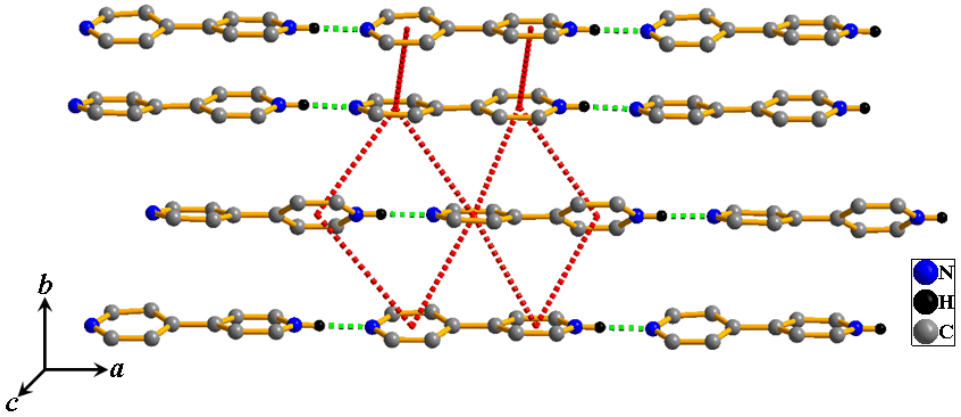

Fig. S3 View of the 2D sheet formed by N-H···N H-bonding (green dashed lines) and π-π interactions (red dashed lines) between the ring centroids of H-bipy cations.

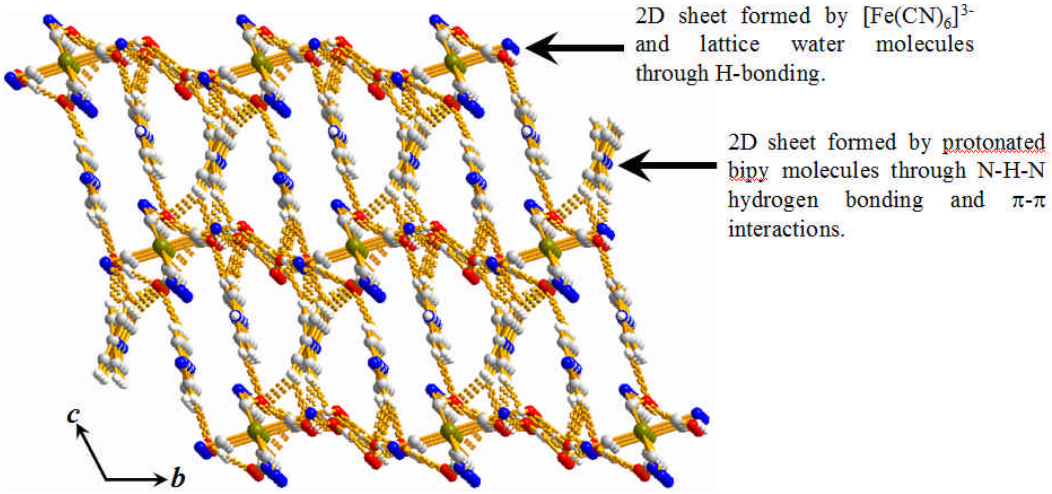

Fig. S4 Figure shows the ABAB type stacking of 2D sheets in host network **1**.

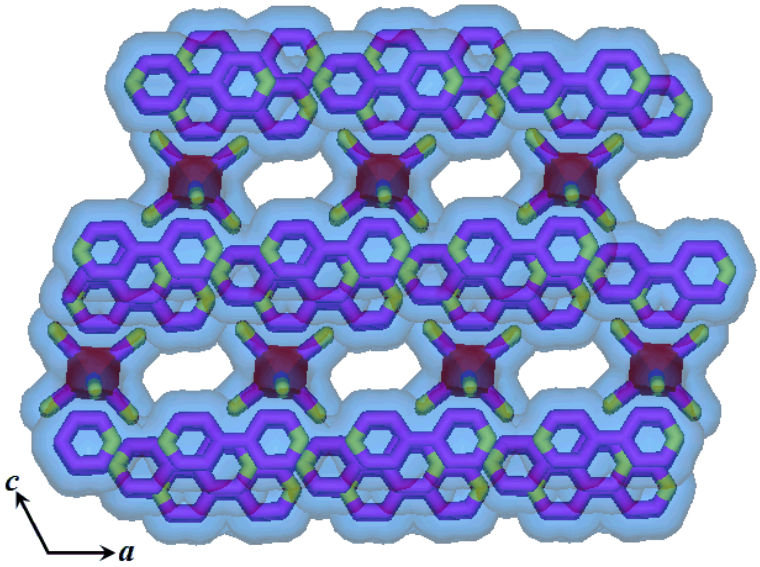

Fig. S5 Surface stick view of supramolecular host **1** after removal of water molecules showing 1D channels of 4.6 x 2 Å along crystallographic *b* direction.

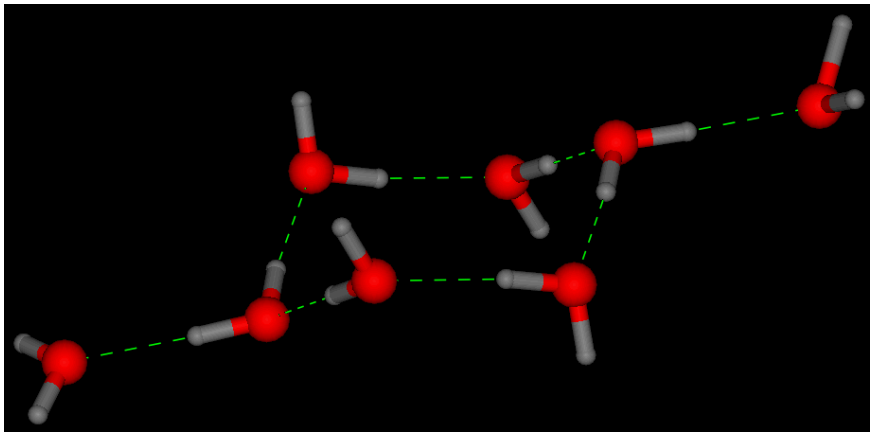

Fig. S6 Optimized configuration of $(H_2O)_8$ cluster with the conformation of *e,e*-1,4-substituted cyclohexane.

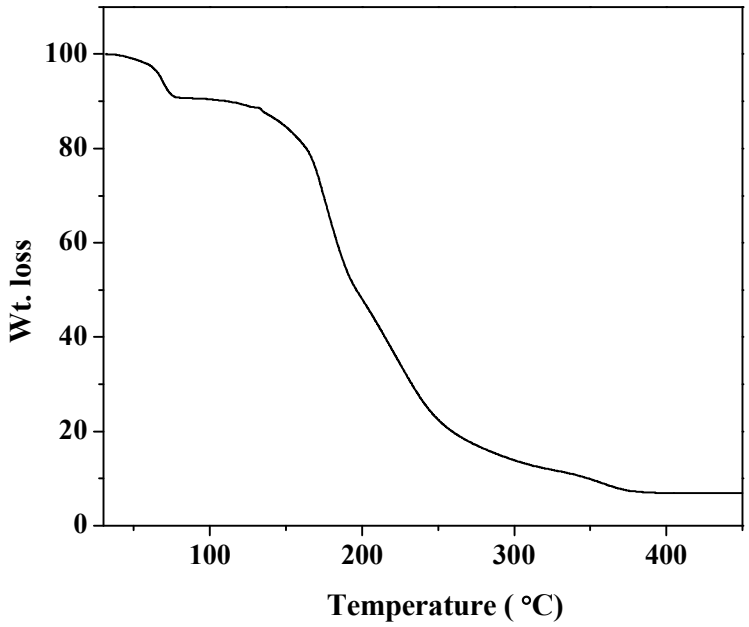

Fig. S7 TGA curve of **1** in the temperature range 30 – 450 °C (Heating rate 5 °C/min under nitrogen).

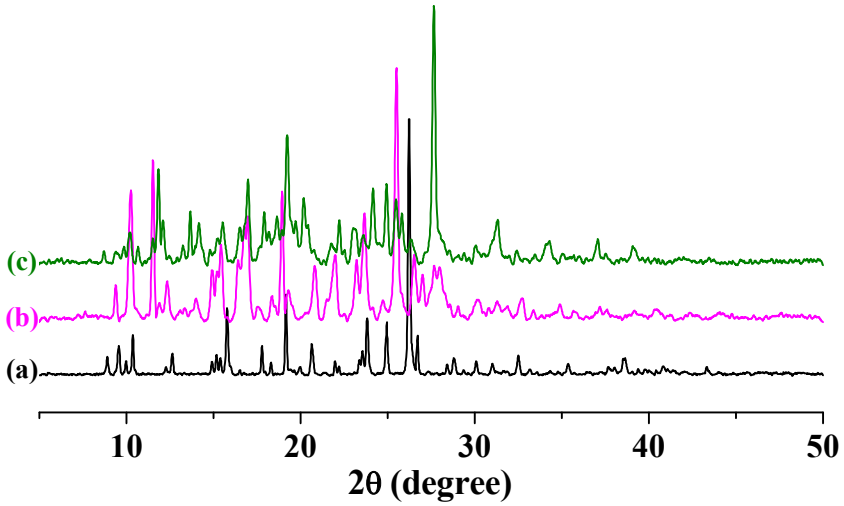

Fig. 8 PXRD patterns of **1** in different state: (a) assynthesized **1**, (b) outgassed at RT for 20h, **1b** and (c) exposed to the water vapor for three days.

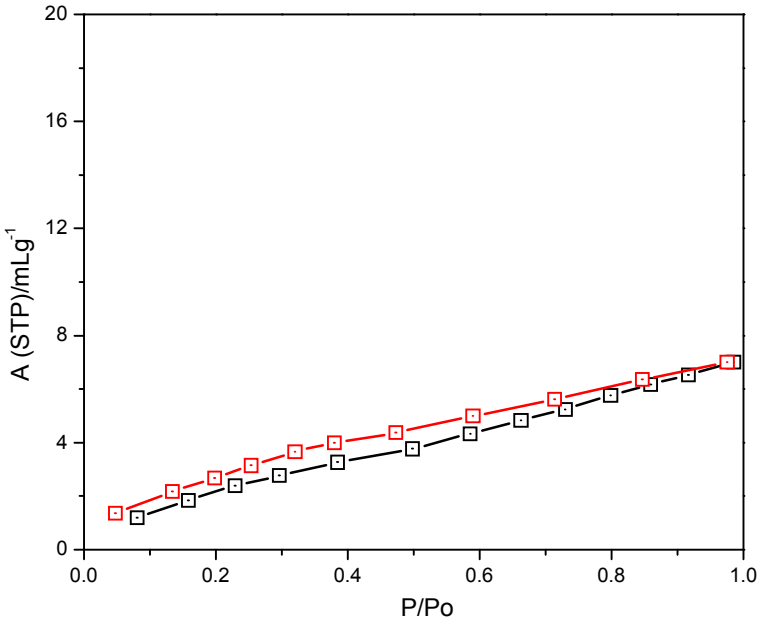

Fig. S9 CO_2 adsorption isotherm of host **1a** measured at 195 K (P_0 is the saturated vapour pressure of CO_2 at 195 K).

Final coordinates for the water cluster

O,0.,0.,0.
H,0.0153242195,0.6660178694,0.6668784345
H,0.8959288231,-0.0884042356,-0.3218835343
O,0.8997097344,2.2436045548,-4.4036713871
H,0.8711729729,1.5605406453,-5.0524207994
H,0.0060787743,2.3569910357,-4.0836894760
O,-4.4226926086,-0.5761642181,-1.2862268586
H,-4.3727686523,-1.4136964542,-0.6643895075
H,-5.1010135179,-1.0851603989,-2.0824837502
O,-1.8298510106,0.0096367816,-2.0022806163
H,-2.7032244927,-0.2097284936,-1.715801127
H,-1.2278856192,-0.0348976488,-1.2659004853
O,2.5789431269,0.0100583466,-0.926739176
H,2.9972726422,-0.6815108696,-1.4111024355
H,2.6744384052,0.8194570897,-1.4343648085
O,-1.643290303,2.2827028222,-3.4987662064
H,-2.0842085397,2.9829867539,-3.0481407854
H,-1.7377734896,1.4877872677,-2.9683579532
O,5.3483640027,2.9690987488,-3.0391402543
H,6.079425146,3.0872013261,-2.438008247
H,5.3889527336,3.4443186114,-3.8302887082
O,2.758005542,2.313091133,-2.3774451859
H,2.1695009122,2.3497405349,-3.1246410106
H,3.6199879969,2.6074301778,-2.6276289827